RESEARCH ARTICLE

Correlations between dynamic fragility, activation energy and glass transition temperature in polymeric composite materials: An overview from literature

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Abstract: Here, it is compiled data from literature for glass transition temperature (T_g) and activation energy (E_a) for different types of polymeric composite materials. A correlation among both parameters and dynamic mechanical curves is analyzed in terms of reinforcement effect and its correlation with the glassy and elastomeric moduli, as well the wideness of the main transition region. Besides, all results are discussed in terms of dynamic fragility. The results indicate that the glass transition temperature has not a direct relation with reinforcement effect promoted both in the glassy and/or elastomeric moduli. Moreover, the dynamic fragility concept seems do not be applied in polymeric composite materials since in the glass transition region the format of the storage, loss and tan delta curves vary strongly, depending on the specific polymeric composite material family.

Keywords: Glass transition temperature; viscoelastic properties; apparent activation energy; dynamic fragility.

1. Introduction

Polymeric composites are complex materials and several factors must be accounted aiming to enhance some specific property, such as filler/matrix interactions, filler dispersion and orientation, reinforcement content and type, among others[1–5]. An attractive characteristic is that the properties of the materials are somewhat different before and after the main molecular transition, i.e., the glass transition temperature/region. So, the application of determined material is directly dependent of the temperature range (of course that it is also dependent of other variables as pressure and environment conditions). If dynamic mechanical properties – in which the mechanical properties can be obtained in a range of temperature - is considered, for example, it is not certain that higher storage modulus in the glassy region will reflect in higher glass transition temperature due molecular chain restrictions imposed by a stronger fiber/polymer interface[2–4,6]. Additionally, the properties can vary of a more drastically way for higher modulus materials when it is achieved higher molecular mobility – the drop of the storage modulus can change sharply in this case[6]. The variation of the properties in the glassy transition region can be correlated with dynamic fragility curves where a more steady change in the drop of the storage modulus represents a dynamic stronger material, i.e., different types of molecular motions (local intermolecular motions and Rouse and sub-Rouse modes) are more separated in the temperature range[7]. This is very important in the science materials field because the manufactured parts are usually used in a range of temperature and an enormous variation of properties can causes catastrophic failures.

So, in the present study we are interested in the relationships between E_a, T_g and the dynamic mechanical curves of polymeric composite materials and correlated them with dynamic fragility concept (which is reflected in the format of

doi: 10.18063/msacm.v2i1.606

the relaxation curves). The motivation for this study comes from so-different dynamic mechanical curves are obtained from polymeric composite materials and many variations can be observed in different regions of the DMA curves. These curves follow different trend depending on the composite type/family. In a study[8], composites with storage modulus on the glassy region of ~100GPa shown practically the same glass transition temperature in comparison to composites with lower storage modulus (1~GPa). Also, the fall drop of the storage modulus of the former is sharper than for the latter. In dynamic fragility's concept, this would indicate that the composite with higher modulus is classified as "fragile" because the variation of modulus occurs rapidly (if it is analyzed the curve format). Furthermore, the same T_g would be indicative that both materials have the same dynamic fragility classification if WLF or VFT equations were applied. So, this classification as applied for different classes of materials: polymers, small molecule organics, hydrogen bonding organics, inorganics, ionic and metallic[9] seems to have a different behavior for polymeric composite materials since in practically all types of material an increase in T_g leads out to an increase in fragility parameter. Therefore, the potential correlation between dynamic fragility and the dynamic mechanical properties of polymers as well T_g and E_a may afford us an alternative way to choose damping materials according to the fragility scale (strong or fragile). In the present study, several kinds of polymeric composite materials were studied based on data from literature.

2. Theoretical review

If it is considered the dynamic mechanical analysis (focus of this study), for example, it is not certain that higher storage modulus in the glass region will reflect in higher glass transition temperature, i.e., higher restriction imposed by the fibers does not shift T_g values for higher temperatures. Additionally, the properties can vary of a more drastically way for higher modulus materials from the glass transition materials[6,8,10–13]. Angell[14] established a concept called dynamic fragility of from the main glass transition temperature (T_g) that evaluates how the chemical structure "degradates", i.e. structural relaxation process occurs. The dynamic fragility refers to dependence of the mass transport or relaxation properties (e.g. relaxation time, viscosity, fluidity) to deviations from Arrhenius behavior. If the materials undergoes a steady change from T_g, the material is called strong. Otherwise, the material is called fragile. Of course that the reference temperature (usually defined as the glass transition temperature, T_g) is dependent of many other factors as pressure and time for example[15]. The fragility, itself is, in fact, a sort of normalized activation energy at the glass transition temperature T_g. This makes it a dimensionless number that in some instances can be useful in bringing behaviors together[16].

Many times it is used the glass transition temperature as a criterion for selection of materials in different applications. This is valid for polymer with similar chemical structure but different arrangements as LDPE and HDPE, for example. In comparing different polymers, some characteristics as molecular structure, free volume, steric hindrance, type of bonds formed in the main chain and laterally, among others are important and give different characteristics of the curve. Specifically it can be risky if the user disconsider the evolution of the molecular mobility with temperature, i.e., how the properties can be modified after the main relaxation process[17–19].

According to previous study from McKenna[16] the dynamic fragility can be directly related to the glass transition temperature by (0.33)Tg[16]. Also, the apparent activation energy at the glass temperature should vary as the Tg^2[16]. The authors mention that there is not an obvious reason to expect that the fragility should be considered rather than E_a for classification of the structural dynamic behavior, since both equations mentioned are based on theoretical basis to the WLF or VFT equations. However, for composites data compiled from literature, since in many cases there are not changes in T_g values itself, it is can be concluded that, in spite of the reinforcement effect in different regions of the relaxation curve (by DMA) the dynamic fragility does not change. This can be due it is effect of the neat resin and polymer/fiber interphase, mainly. So, in analyzing the dynamic mechanical curves format (storage, loss and tan delta)[7] it is can be noted differences for many composites after T_g maximum, which equation would not applied – in this case, it is analyzed the curve format and not a single temperature point.

For composite materials this task seems to becomes harder. When glassy polymers are used as matrix in composite materials, the issues surrounding the glassy behavior of the polymers is highly important in determining the ultimate

performance of the composite material essentially because the polymer matrix is frequently the weakest link in the composite. In addition, since a polymeric material is reinforced with fibers or fillers, the interactions of the reinforcement with the matrix can alter the behavior of the resin, and this can have consequences for the expected behavior of the composite material. What is responsible for the T_g it is the matrix component, i.e., the polymeric material. If the fiber/filler does not interferes someway in the matrix, no changes will be observed[20]. But reinforcement can improve some mechanical properties in the glassy region, but not necessarily will improve the glass transition or even interpheres in the elastomeric modulus necessarily. In the study of Almeida's[8] epoxy/carbon composites transversally and horizontally oriented were studied in relation to creep resistance. T_g practically maintains similar values at different angle plies (from 0 º to 90º). The main difference is after the maximum tan delta peak; the properties vary more drastically for composite with higher modulus. What differs polymeric composite materials from other materials is that depending on the matrix used (thermoplastic, thermosetting or rubber), the reinforcement effect can be improved in the storage modulus in the glass region or increase the temperature range which the material can be used, i.e., shift T_g for higher temperatures. Many other studies present similar trend[2–7,10–13]. So, the results suggest that there are not a direct relation among the glass transition values and the reinforcement effect (after or before the main transition) and the use of T_g as an estimative of the "resistance" of the material can leads to an oversimplification of the system.

2.1 Glass transition temperature

From a practical point of view, the glass transition is a key property because it corresponds to a temperature above there is a catastrophic softening of the material. In a narrow temperature range, the material goes from a liquid-like mobility to a nearly solid behavior[21]. In most of cases, T_g is represented as a maximum peak of the main event (tan delta curve), so in most of the cases, as a unique temperature[15,18–19], neglecting the extension of the relaxation process. For industrial purposes, it is used as the temperature where the material starts to softening, so it becomes very important for processing conditions as extrusion process for example. From a scientific point of view, it is know that the apparent mobility process comprehend a wide temperature range. It can be divided in two main sections: i) near and somewhat below T_g – structural relaxation, annealing and aging and ii) rather far below T_g – constant structure relaxation ("frozen structure") and its implications[18]. Here we discussed about structural relaxation.

The glass transition temperature is in a non-equilibrium state with two linear dependences on temperature process, i.e., the intersection of the two straight-line regimes. When the polymeric material is formed (vitrification) from the liquid state, since it is impossible to vitrify uniformly, inhomogeneities are formed, leading out to a thermodynamic non-equilibrium state[17–19,22]. As the liquid is cooled, molecular mobility decreases (due lower thermal excitation), reflecting in a decreasing in the relaxation time/viscosity as proposed by the well-known equation used in polymer field Williams-Landell-Ferry (WLF):

$$\log a_T = \frac{C_1(T - T_g)}{C_2 + T - T_g} \tag{1}$$

where a_T is the temperature shift factor, C_1 and C_2 are material constants. C_1 constant has a physical meaning because is the number of orders of magnitude between the relaxation time at the glass transition temperature and the pre-exponent of the VFT equation (on T_g is obliged to have the value of 16-17, depending on how the glass transition temperature is defined). So C_2 will reflect the non-Arrhenius character or fragility of the system[23]. Many correlations among these parameters were established successfully using WLF, VFT, activation energy, glass transition temperature and dynamic fragility[9,22,23].

2.2 Glass transition temperature definition

Here we start to define the glass transition temperature as described by Williams[18] as "a boundary surface in a

tridimensional space defined by temperature, time, and stress separating the glass and rubbery (or liquid) domains". It comprehends a wide range of temperature and not a unique point. The reason is that polymeric chain has distinct parts that respond differently when thermally stimulated, so the potential barrier to overcome any translational movement can differs strongly. In general, more structural heterogeneity/or dynamically strong is the material, broaden is the curve of the relaxation spectrum. In molecular terms, greater the difference between the local relaxation process and the Rouse and sub-Rouse modes broadens the relaxation process[7]. There are several techniques for determination of the glass transition values: differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA). Since most of the physical properties of the polymer (heat capacity, expansion coefficient, storage modulus, gas permeability, refractive index, etc.) undergo a discontinuous variation at the glass transition and T_g is usually characterized as a second-order thermodynamic transition[15] is it led to the readers to choice the better/available technique.

2.3 Thermodynamic or kinetic approach?

It is important to mention that still there are divergent viewpoints that attempts to describe a well-defined set of physical phenomena about the glass transition. Such viewpoints fall into two broad categories: purely thermodynamics or kinetics. We have to start to think that is a kinetic slowdown experienced by liquids as they are cooled toward their glass transition and this slowdown is not accompanied by any obvious structural change. Considering only thermodynamic process occurring, the glass transition is caused by rapid loss of entropy in the supercooled liquid (cooled before vitrification) underlies kinetic slowdown. In considering only kinetic approach, purely kinetic constraints are responsible for loss of ergodicity[22].

The glass transition conserves a liquid-like disorder but with solid-like properties. As the liquid is cooled, molecular mobility decreases (lower thermal excitation), reflecting in a decreasing in the relaxation time/viscosity as proposed by Eq. (1). The slowdown of the molecular mobility becomes infinite a temperature below the glass transition temperature but above absolute temperature. In a narrow temperature range, the material goes from a liquid-like mobility to a nearly solid behavior[17,18,23].

Huang and McKenna[24] studied the correlation of thermodynamic and dynamic fragilities (thermodynamic and dynamic approaches) for polymeric systems and the results suggest a certain inconsistency of the results but a slight trend to dynamic fragility increases by decreasing of the thermodynamic one. Cangialosi et al.[25] suggest that the presence of relaxation processes unrelated (such as intramolecular motions) of the main relaxation process which contributes to global properties of some polymers offers a plausible explanation to the inability of other approaches to maintain a clear correlation between relaxation time and excess entropy. So, inconsistencies are expected since dynamic fragility is merely related to the α-relaxation process (T_g) and thermodynamic fragility (excess entropy) is representative of the overall structure of the polymer.

2.4 Apparent activation energy

According to Q. Qin and McKenna[9], the dynamic fragility for polymeric materials displays a roughly linear correlation with the glass transition temperature, i.e., the material with higher glass transition temperature tends to behave in a more fragile fashion. The fragility for polymers covers a large range from about 40 to more than 200, being for the most of polymers exhibiting values in the range $100 < m < 220$. Polymers that have very flexible and symmetric chain backbones has a strong m value and lower T_g values. Polymers containing compact chain backbones tend to have a nearly Arrhenius temperature dependence of segmental relaxation, while polymers having less flexible backbones, their temperature dependence of segmental relaxation exhibits fragile behavior. The correlations between m and T_g and E_a and T_g can be found on McKennas' study[16]. The apparent activation energy seems to varies as the square of the T_g which is consistent with the WLF-type of free volume ideas as first suggest by Kovacs, as mentioned the author.

2.5 Dynamic fragility

In the 1980s, Angell expanded the concept of fragility for glass-forming liquids. The dynamic fragility refers to

deviations from Arrhenius temperature dependence of mass transport or relaxation properties (e.g., relaxation time, viscosity, fluidity). Strong liquids follow the Arrhenius behavior while fragile ones exhibit VFT or WLF behavior. The dynamic fragility or steepness index characterizes the rapidity with which a liquid's dynamic properties change as the glass transition temperature is approached and is quantified as[14,24,25]:

$$m = \left[\frac{d \log x}{d\left(\frac{T_g}{T}\right)} \right]_{T=T_g} \tag{2}$$

where x can be viscosity, relaxation time or other dynamic variable. Importantly, the dynamic fragility is effectively a T_g- normalized activation energy.

In an earlier work, Qin and McKenna[16] studied a wide variety of glass-forming liquids, and concludes that polymer materials displays a roughly linear relationship between dynamic fragility and the glass transition temperature, and their activation energy at T_g varies approximately as T_g^2. This conclusion leads the authors to propose a new fragility index as described in Equation (2):

$$m_2 = \frac{E_g}{T_g^2} \tag{3}$$

where m_2 is the fragility index, E_g (kJ.mol^{-1}) is the activation energy and T_g^2 (K) is the glass transition temperature raised to square.

In an earlier study of Wu[7] normalized dynamic mechanical curves were studied and correlated with the dynamic fragility without use of dielectric measurements. The results obtained can be easily and directly (without invoke any mathematical treatment) interpreted, giving us an idea of the temperature dependence of dynamics for these materials.

If the correlation between the dynamic fragility and the glass transition temperature gives us not a satisfactory correlation coefficient for polymeric glass formers, for composite materials is not different. In the latter, the absence of data from literature do not allows knowing precisely this dependence for composite materials. There will not be changes in the composite behavior in relation to the neat resin unless the fibers somehow interact with the polymer resin to change the aging response of the resin[20]. Having this in mind, if there are interactions between the fiber and the resin, lower will be the temperature dependence of their dynamics. Also, some properties cannot be easily mapped. Even if there is not adhesion between matrix/fiber, the reinforcement can dwells the reticulation, providing interactions in the formation of the network and having consequences in the expected behavior of the composite material. In other cases, the reinforcement can act as an impurity, acting as a plasticizer, and so softening the material.

Of the few studies about dynamic fragility on composite materials it can be cited Gregorova's[26]. The authors study the effect of hydrothermal modification, maleic anhydride treatment, silane and stearic acid surface treatments on viscoelastic properties of spruce wood flour filled PLA composites. It occurs the decrease in dynamic fragility due to the treatments of wood flour indicating, in this case, positive effects on the interfacial compatibility between treated wood flour and PLA. So, in this case, the dynamic fragility improvement was related to interfacial compatibility between fillers and PLA, with differences in the glass transition temperatures. Kwon *et al*[27] studied the fragility index of nano- and micron-silica particles bidispersed epoxy composites and the results suggested that an increase in the content of nanoparticles gave rise in a decrease in the fragility of the composites. The reduction in interparticles distance caused the particle-matrix interactions to induce heterogeneity in the matrix expressed as decreasing fragility. So the decreasing of m with high particle composition showed the relationship between the

heterogeneity in epoxy matrix and the interphase distance. In both cases, there are changes in the dynamic fragility due changes in the α-relaxation process, i.e, increasing/decreasing of T_g.

3. Results

Table 1 below showed some of glass transition temperature and the activation energy values from different composite materials containing different reinforcement contents, hybridization effect, and fiber length, among others.

Composite	T_g (°C)	E_a (kJ.mol^{-1})	References
Isophthalic polyester resin	130	-	[28]
Isophthalic polyester resin/40% banana fiber/1%NAOH	133	75	[28]
Isophthalic polyester resin/40% banana fiber/0.5%NAOH	142	32	[28]
Isophthalic polyester resin/40% banana fiber/Silane 1	133	32	[28]
Isophthalic polyester resin/40% banana fiber/Silane 2	139	42	[28]
Isophthalic polyester resin/40% banana fiber/Acetylated	137	39	[28]
Isophthalic polyester resin/40% banana fiber/Non-treated	137	41	[28]
PMMA	87.7	-	[29]
PMMA/1% keratin fiber	93	-	[29]
PMMA/2% keratin fiber	88.5	-	[29]
PMMA/3% keratin fiber	87.8	-	[29]
PMMA/4% keratin fiber	98.7	-	[29]
PMMA/5% keratin fiber	96.1	-	[29]
Epoxy	-	564.5	[30]
Epoxy/SAN/10% glass fiber	-	565.5	[30]
Epoxy/SAN/20% glass fiber	-	575.2	[30]
Epoxy/SAN/30% glass fiber	-	583.2	[30]
Epoxy/SAN/40% glass fiber	-	658.8	[30]
Epoxy/SAN/50% glass fiber	-	689.5	[30]
Epoxy/SAN/60% glass fiber	-	577.8	[30]
PP	-	3.9	[31]
PP/10% sisal fiber	-	2.9	[31]
PP/20% sisal fiber	-	5.6	[31]
PP/30% sisal fiber	-	5.6	[31]
PP/20% sisal fiber 2mm	-	5.8	[31]
PP/20% sisal fiber 10mm	-	5.6	[31]
PP/20% sisal fiber 6mm TDI	-	5.9	[31]
PP/20% sisal fiber 6mm Maleic Anhydride	-	6.0	[31]
PP/20% sisal fiber 6mm KM_nO_4	-	6.0	[31]
Isophthalic polyester resin	114.4	25.7	[32]
Isophthalic polyester resin/10% banana fiber	106	21	[32]
Isophthalic polyester resin/20% banana fiber	112	23.8	[32]
Isophthalic polyester resin/30% banana fiber	107	22.8	[32]
Isophthalic polyester resin/40% banana fiber	125.3	41.2	[32]
Isophthalic polyester resin	-	53	[33]
Isophthalic polyester resin/19% sisal/banana	-	65	[33]
Isophthalic polyester resin/32% sisal/banana	-	67	[33]
Isophthalic polyester resin/40% sisal/banana	-	68	[33]

Isophthalic polyester resin/48% sisal/banana	-	68	[33]
Isophthalic polyester resin/40% banana	-	67	[33]
Isophthalic polyester resin/40% sisal	-	51	[33]
Epoxy/15% quartz powder	-	493	[34]
Epoxy/25% quartz powder	-	498	[34]
PS	-	348.5	[35]
PS/10% sisal 6mm	-	338.5	[35]
PS/20% sisal 6mm	-	351	[35]
PS/30% sisal 6mm	-	392	[35]
PS/30% sisal benzoylated 6mm	-	402.9	[35]
PS/30% sisal acetylated 6mm	-	349.4	[35]
PS/30% sisal PSMA 6mm	-	392.4	[35]
PS	109.3	-	[36]
PS/10% wood floor	107.6	-	[36]
PS/20% wood floor	108.8	-	[36]
PS/30% wood floor	109.2	-	[36]
PS/40% wood floor	109.7	-	[36]
Isophthalic polyester resin	110.9	331.4	[37]
Isophthalic polyester resin/curaua/glass 100/0	113.2	307.4	[37]
Isophthalic polyester resin/curaua/glass 75/25	116	280.1	[37]
Isophthalic polyester resin/curaua/glass 50/50	115.8	291.6	[37]
Isophthalic polyester resin/curaua/glass 25/75	117.1	345.1	[37]
Isophthalic polyester resin/curaua/glass 0/100	118	353.5	[37]
Polyester	80.1	248.9	[38]
Polyester/sisal/glass 10/100/3	80.8	176.9	[38]
Polyester/sisal/glass 10/75/3	82.6	223.9	[38]
Polyester/sisal/glass 10/50/3	83.6	234.8	[38]
Polyester/sisal/glass 10/25/3	84.9	237.6	[38]
Polyester/sisal/glass 10/100/4	79.9	161.8	[38]
Polyester/sisal/glass 10/75/4	82.2	217.5	[38]
Polyester/sisal/glass 10/50/4	83.2	231.5	[38]
Polyester/sisal/glass 10/25/4	85	235.6	[38]
Polyester/sisal/glass 20/100/3	82	201.6	[38]
Polyester/sisal/glass 20/75/3	83.2	238.4	[38]
Polyester/sisal/glass 20/50/3	84.7	243	[38]
Polyester/sisal/glass 20/25/3	85.3	254.3	[38]
Polyester/sisal/glass 20/100/4	82.2	205.6	[38]
Polyester/sisal/glass 20/75/4	83.5	235.4	[38]
Polyester/sisal/glass 20/50/4	84.4	246	[38]
Polyester/sisal/glass 20/25/4	86.1	260.5	[38]
Polyester resin	110.9	331.4	[2]
Polyester/ 11% curaua	113.2	310.4	[2]
Polyester/ 22% curaua	113.4	307.4	[2]
Polyester/ 32% curaua	110.2	293.9	[2]
Polyester/ 38% curaua	112.1	278.9	[2]
Polyester	115	-	[39]

Polyester/glass/ramie 0/100	116	354	[39]
Polyester/glass/ramie 25/75	112	414	[39]
Polyester/glass/ramie 50/50	112	419	[39]
Polyester/glass/ramie 75/25	113	421	[39]
Ortophthalic polyester/curaua/glass 30/100/0	101.8	-	[40]
Ortophthalic polyester/curaua/glass 30/70/30	119.9	-	[40]
Ortophthalic polyester/curaua/glass 30/50/50	119.1	-	[40]
Ortophthalic polyester/curaua/glass 30/30/70	118.6	-	[40]
Ortophthalic polyester/curaua/glass 30/0/100	112.3	-	[40]
PP/60% pinus wood floor/2% PP-gam	14	373	[41]
PP	5.03	10	[42]
PP/10% banana fiber	6.38	12.5	[42]
PP/30% banana fiber	8.29	15.7	[42]
PP/50% banana fiber	8.35	16.3	[42]
Phenol Formaldehyde (PF)	143	14	[43]
PF/30% oil palm fiber 40mm	148	308	[43]
PF/40% oil palm fiber 40mm	138	63	[43]
PF/50% oil palm fiber 40mm	119	15	[43]
PF/glass fiber/oil palm fiber 100/0	94	78	[43]
PF/glass fiber/oil palm fiber 70/30	95	108	[43]
PF/glass fiber/oil palm fiber 50/50	89	20	[43]
PF/glass fiber/oil palm fiber 30/70	97	50	[43]
PF/glass fiber/oil palm fiber 10/90	94	17	[43]
PF/glass fiber/oil palm fiber 8/92	90	41	[43]
PF/glass fiber/oil palm fiber 4/96	91	20	[43]
PF/glass fiber/oil palm fiber 0/100	138	63	[43]
Polyester	116	-	[44]
Polyester/pineapple leaf fiber/glass fiber 100/0	143	106.1	[44]
Polyester/pineapple leaf fiber/glass fiber 90/10	130	210.9	[44]
Polyester/pineapple leaf fiber/glass fiber 80/20	115	314.9	[44]
Polyester/pineapple leaf fiber/glass fiber 70/30	121	207.7	[44]
Polyester/pineapple leaf fiber/glass fiber 50/50	139	104.4	[44]
Epoxy/carbon sheet	63.3	366	[45]
Epoxy/carbon sheet	78	408	[46]
PHBHB with 3.2 %vol. nanohydroxyapatite	17.1	350.2	[47]
PHBHB with 9.1 %vol. nanohydroxyapatite	17.3	351.9	[47]
PHBHB with 14.2 %vol. nanohydroxyapatite	17.6	372.9	[47]
LLDPE 10% oil palm fiber alkali – treated	-127	55.8	[48]
LLDPE 30% oil palm fiber alkali – treated	-115	72.6	[48]
LLDPE 40% oil palm fiber alkali – treated	-118	66.6	[48]
LLDPE 30% oil palm fiber alkali – non-treated	-115	70.7	[48]
Epoxy 40% glass spheres saturated in water	116.8	112	[49]
PLA 20% wood flour	51	189	[50]
PLA 20% wood flour 0.5 MDI	52	249	[50]
PLA 20% soy flour	53	310	[50]

PLA 20% wood flour 0.5 MDI	53	287	[50]
Natural rubber 30% oil palm fiber	-45.8	258.12	[51]
Natural rubber 30% silanized oil palm fiber	-44.01	369.68	[51]
NBR 2% CNT	-12.2	-	[52]
NBR 5% CNT	-13.7	-	[52]
NBR 10% CNT	-12.7	-	[52]
NBR 15% CNT	-11.8	-	[52]
SBR 2% CNT	-40.5	-	[52]
SBR 5% CNT	-41.6	-	[52]
SBR 10% CNT	-40	-	[52]
SBR 15% CNT	-39.2	-	[52]
EPDM 0.1% vol. $Al(OH)_3$ 24.2 microns	-46.8	68.2	[53]
EPDM 0.1% vol. $Al(OH)_3$ 24.2 microns- treated	-46.2	74.8	[53]
EPDM 0.1% vol. $Al(OH)_3$ 1.25 microns	-45.7	71.5	[53]
EPDM 0.1% vol. $Al(OH)_3$ 1.25 microns- treated	-45.3	76.7	[53]
PP 0.1249% V cotton fiber	-	33.87	[54]
PP 0.1249% V cotton fiber treated with KmnO4	-	37.84	[54]
PP 0.1249% V cotton fiber treated with MAPP	-	40.55	[54]

Table 1. Glass transition temperature and activation energy values for different types of composite materials obtained from literature.

Aiming to better visualize the data above, it was plotted the data of T_g vs E_a for the composites in which both parameters were presented (**Figure 1**):

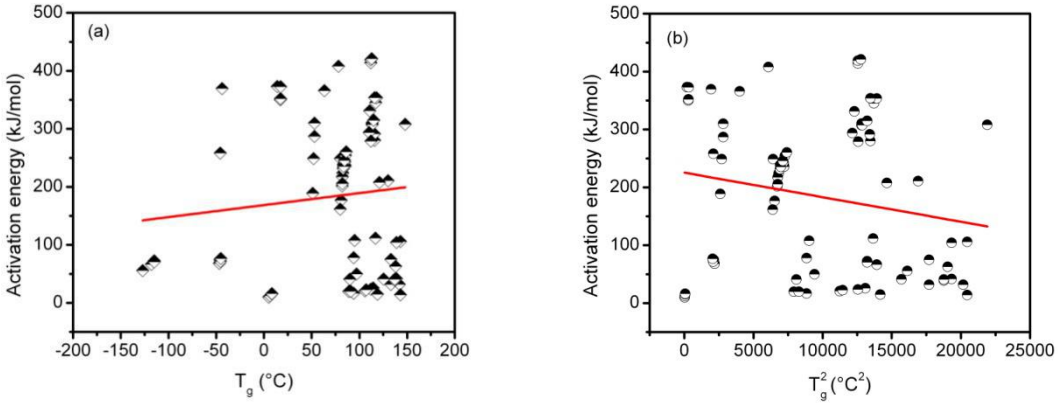


Figure 1. Plot of the glass transition temperature vs activation energy values for polymeric composite materials (the solid line through data represents a guide for the eyes).

The results suggest that both parameters do not follow any significant trend for any class of polymeric composite materials observed. So, the application of the fragility parameters as presented in Equation (3) will not follow any clear trend and so will not be presented in the current study.

The results for the data above do not showed a dependence of the activation energy with the glass transition temperature as it can be previous observed for polymeric materials[9]. Also, the second order polynomial fit to the data observed for polymeric materials[9] as E_a varies approximately at T_g^2 is not observed for our results. So, Equation 3, for example in which correlate dynamic fragility with activation energy and the glass transition temperature seems not to be applicable for polymeric composite materials – or if applicable must be done carefully.

The reader has to have in mind that the activation energy and the glass transition temperature were obtained from the glassy region where molecular mobility takes place. Even if the values do not showed significant differences in general, in other regions (as the glass region or the elastomeric region) the reinforcement effect can be much more

evident. For example: a composite system can have practically the same T_g value but differences of 4-6 order of magnitude in the glassy region[8]. By the other hand, the reinforcement effect in the elastomeric region can do not alter by reinforcement with alterations in the glass transition temperature[6]. So, each composite material has to be studied carefully and the present authors do not identify any "general rule" about it. Trying to elucidate the reader, in Discussion Section it was separated the main characteristics of the dynamic mechanical curves obtained from literature, which can represent the reinforcement effect. The characteristics will be discussed separately: i) glass transition temperature as a reference temperature ii) the fall drop of the storage modulus iii) decay between the glassy and elastomeric states iv) the width of the relaxation spectra v) peak height and vi) relaxation area and vii) activation energy.

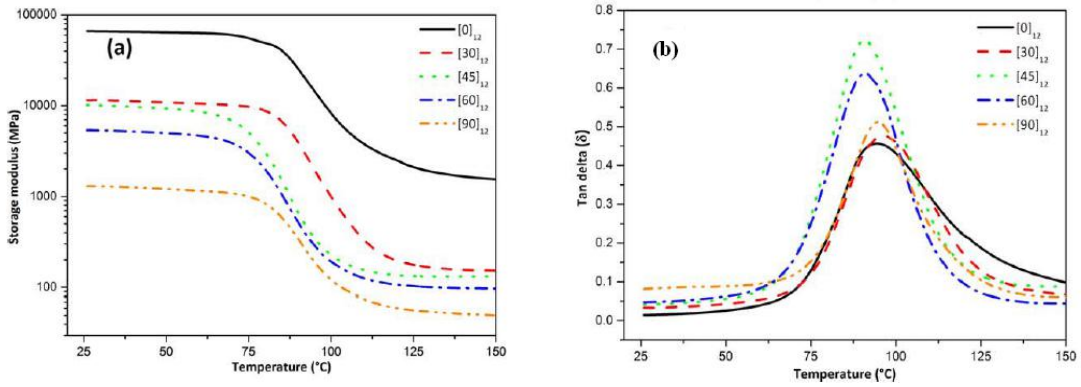
4. Discussion

The well-established VFT and WLF equations are based in well–based physical models and they usually give and quantitative comparison among polymers due differences in their chemical structure, as an example. Through these models, correlations between glass transition temperature and activation energy values and as consequence, values for the dynamic fragility index m can be estimated. However, for composite materials, the values obtained using these models are not necessarily indicative of the characteristics of such material (as is more clearly observed for polymers) since so many variables are involved in a composite material such as fiber/matrix interactions, type of reinforcement or angle ply disposition, for example as showed so far. In applying the equations as proposed by Hung and McKenna[9] aiming to determine the fragility index, the results (not showed here) obtained are not satisfactory and deviate a lot from the expected ones. Some of the values are even lower than from the stronger polymeric glass forming materials found on literature (m ~ 23 for poly(oxyethylene)). In our opinion, the main question of the unexpected values is that the models applied are based on free volume ideas. Also, it can be interpreted in terms of coupling model as proposed by Ngai[55,56], where polymers with smooth, compact chain backbones tend to have a nearly Arrhenius temperature dependence of segmental relaxation, while for polymer having a less flexible backbones, their temperature dependence of segmental relaxation exhibits fragile behavior. Correlations between dynamic fragility and T_g in polymers with varying molecular weights and crosslink densities were observed in literature[57–61]. In all cited works[55–61], fragility changes in the same direction as T_g does.

For composites, besides free volume and chemical structure, interactions between fiber and matrix (interphase) plays a major role in the relaxation process, becoming a very hard task to find a "chemical structure response" for these materials. By the other hand, a single quantitative behavior without considering any molecular structure using the curve format can be considered for comparison. Also, the behavior of T_g in composite materials can be attributed to the polymeric matrix and how the fiber can retards the relaxation process (shifting the transition for higher/lower temperatures). For polymeric materials change in the main relaxation process usually promotes changes in the dynamic mechanical behavior of the curve (be in the glassy or elastomeric modulus). So higher T_g for determined polymer due a more efficient chain packing, for example, would reflect in higher glassy modulus. But in polymeric composite materials, no trend can be observed in observing different systems.

There are some "main problems" in analyzing dynamic fragility for composite materials: i) glass transition temperature as a reference temperature – it is know that T_g is used as a reference point for estimation of the dynamic fragility. So, in normalizing the maximum of the relaxation spectra as a reference, the behavior of the curve after this maximum will reflect the "resistance to chemical structural degradation" of the sample. The main problem is that for some classes of composite materials those values remain similar as the reinforcement content is increased (in glassy or elastomeric regions the difference in modulus is easily observed – but not always). So, it is becomes clear that the glass transition temperature does not reflect how the reinforcement is effective, mainly in the α-relaxation process. As examples it can be cited some studies[1–6,8] where the reinforcement was considerable in the glassy or elastomeric regions but T_g peak maximum remains practically unaltered. So, the behavior from this point must be considered, i.e. how the relaxation curve decreases (i.e. smoothly or sharply); In Figure 2 it can be noted that the maximum peak of the tan delta curve (Figure 2b and 2d) does not show significant differences at different angle plies, showing that the glassy region (Fig 2a and 2b) values has not direct influence on T_g values. But in this case higher elastomeric modulus values

were obtained for transversally oriented angles. ii) the fall drop in the storage modulus – the glassy state reflects the local molecular motion (Brownian motion) and so, until the beginning of the fall drop of the storage modulus. After, sub-Rouse and Rouse relaxation modes play a major role. Wu[7] in normalizing storage modulus curves noted that for dynamic stronger materials, the fall drop of the storage modulus is smoother, because the chemical structure is more time/temperature resistant. This means that, if we think about the chain packing efficiency, better packing causes lower free volume, and so higher modulus on the glassy state would be obtained, which would extend the glassy region range. The force of the intermolecular forces also contributes for that. When the polymer begins the fall drop of the storage modulus, the decay of the curve would be smoother because changes in molecular conformation would occur slower with temperature (more efficient chain packing). By the other hand, a poor chain packing efficiency allows that the molecular conformation in the glass transition region occurs rapidly, and so, the curve would be of a sharp format. The first case is characteristic of stronger materials while the latter is of fragile's. In molecular terms, it reflects how the relaxation modes are influenced, i.e., if the relaxation of the chain segments are greater, smoother will be the decay of the curve because they are more separated from each other in time/temperature scale. For composite materials, in comparing different composites (same polymeric matrix and varying the fiber content) it is noted two distinct behaviors a) in some cases [Figure 2c], the storage modulus curve decreases smoother with temperature, b) and in other case (structural composites, mainly) [Figure 2a] this fall drop is of some orders of magnitude and decreases more abruptly. Here, it is clear that the fall drop of the curve for composite materials can differs strongly. Figure 2a) it is noted a difference of almost 70000 MPa for [0º] for 1000 MPa for [90º] in the glassy storage modulus. Even so, the range of the glassy region remains almost the same for both materials and it can be noted (at least visually) that the fall drop is very similar in both cases as T_g (Figure 2b)). In Figure 2c) can be noted that higher difference is obtained for neat resin (with lower storage modulus) with a more abrupt fall drop in the glassy region. However, Figure 2d) shows higher T_g values for neat resin, indicating that there are no direct relation between the fall drop in the glassy region and the glass transition values. In molecular terms, it seems that the local molecular motion is affected, or more precisely, the interface between matrix and fiber becomes more effective. This means that great part of the stress imposed in the composite is transferred from the matrix for the fiber, which absorbs great part of it. Poorer the interface, more energy is dissipated and the fibers can, in some cases, act as impurities, decreasing significantly the modulus. So, the fall drop will depend on how the energy will be dissipated along the glassy region. If the energy is dissipated at once, the curve decay will be sharply format.



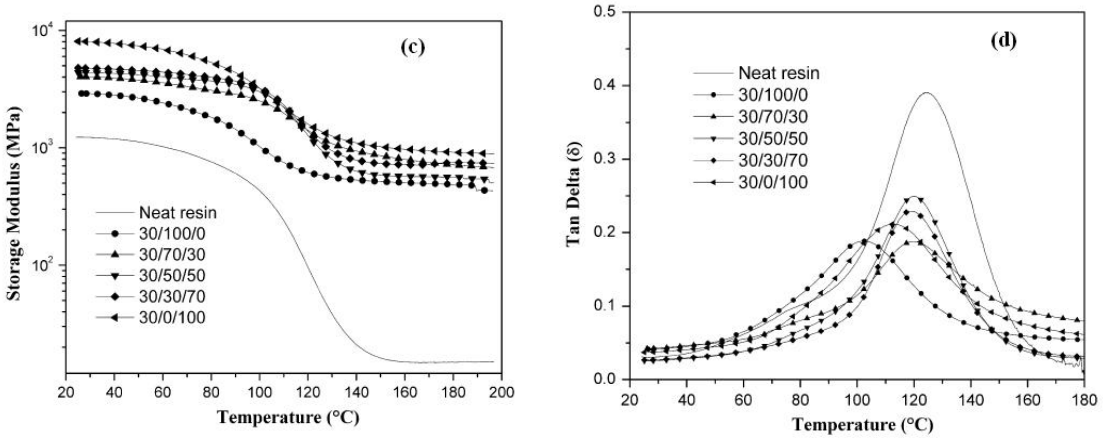
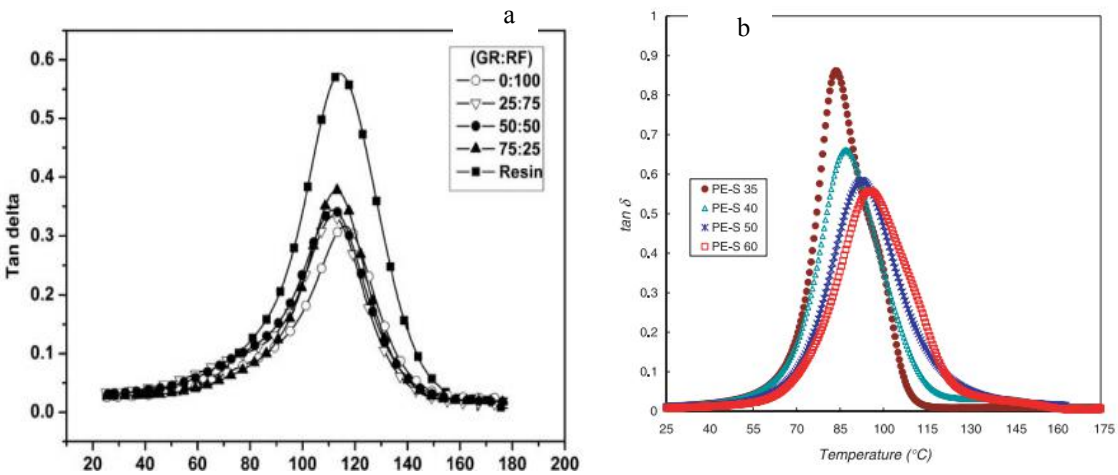


Figure 2. Storage modulus and tan delta curves for different oriented angle plies epoxy/carbon fibers (adapted from[8] and reproduced with permission from[40]).

iii) difference range between the glassy and elastomeric states – the effectivety of the reinforcement can be estimated in calculating how the modulus value is "lost" or decrease from a chosen reference temperature (coefficient of reinforcement). The reinforcement in some cases is only effective in determined temperature range or specific region. If the reinforcement is effective (in the glass transition region, for example) the difference range is lower between both glass and elastomeric regions. Sometimes occurs that the reinforcement is so effective in the glassy region leading out to higher modulus values and so many energy is storage that when molecular motion takes place, that amount of energy is released at once, causing similar modulus in the elastomeric region. For composites, which do not storage so many energy in glassy region, lower dissipation is expected in the glassy transition region and so lower difference between modulus in the glassy and elastomeric region is expected. This is important because if the difference is enormous between both regions a catastrophic failure can occur in the composite iv) the width of the relaxation spectra – for polymers, this parameter can be interpreted in terms of dynamic fragility. Stronger materials show broader curves while fragile materials show narrow curves[62]. The main transition for amorphous polymers from the glassy state to the elastomeric region involves different modes of molecular motion, including local movement (Brownian motion), sub-Rouse and Rouse model, which differs from each other as mobile unities becomes higher, respectively[7,63]. Also, a better packing causes lower free volume (as cited earlier), which retards the molecular motion from higher chain segments to an extension from local chains. As a result, the motion of long chain segments with different sizes are separated from each other in time/temperature scale, which causes a broadening in the relaxation spectrum. In strong polymers, the sub-Rouse and Rouse models are apart from the Brownian motion in a time/temperature scale[7].



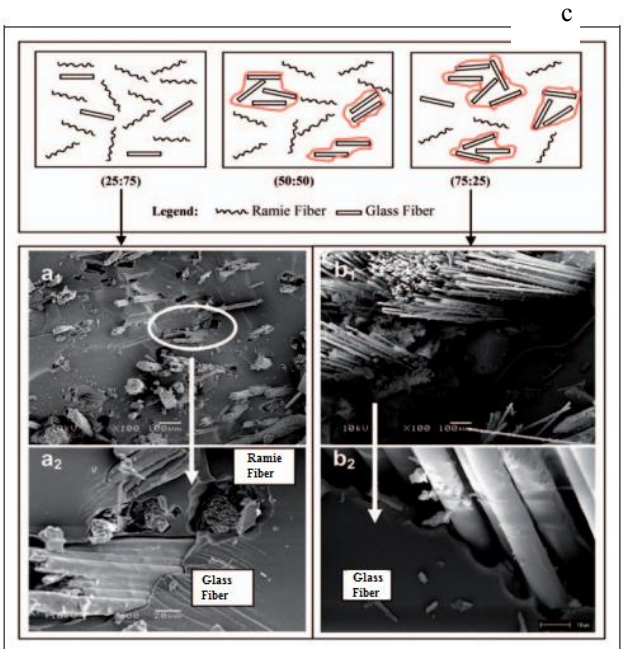


Figure 3. a) Tan delta curve for polyester containing different styrene contents, b) Tan delta curve for and micrography for ramie/glass fiber composites [adapted from[63] and[39].

For composite materials, again, two distinct behavior were already reported on literature: a) broader of the curve by reinforcement incorporation and b) vice-versa. In both cases, it can be related to the distribution of the reinforcement on the matrix, polymer/fiber interface and fiber content. If the reinforcement is well distributed/disperse and the system homogeneous, it can causes two possible features: 1- higher modulus in the glassy region which probably will extend the glassy region for higher temperature/time follow of a rapidly decreasing of the storage modulus due, since higher energy is storage, higher energy will be dissipated; 2- differences in the relaxation process (Fig 3c), i.e., some portions of the material are heterogeneous (some parts richer in resin meanwhile other richer in fiber) and a poorer interface. In the latter the energy storage is not so high, and the energy is dissipated in low amounts. The interphase that hindrances the mobility of the resin around the fibers is not so tight, making the curve decrease smoother v) peak height – is related with the energy dissipated as heat in the relaxation process[55,57,59,6,62]. Lower peak height means a more effective interphase because the energy is storage in the interphase. But it can occurs that if the energy is dissipated at low amounts in the time/temperature range, the width curve can be extended generating a lower peak height, but a broader width. In some cases, it can generate a higher peak – if there is a poor interphase, because the fiber will not maintain the strain received vi) relaxation area – the relaxation area gives us an idea of the homogeneity of the system[37]. In some examples, the peak height is higher but it is compensated by a lower peak width and vice-versa, so the final relaxation area can be the same. A more valid comparison would be peak height if the width would the same, but it is very difficult this phenomenon occurs. Higher values would mean a broader distribution of the relaxation times (strong polymer), while narrow ones would mean a fragile polymer as mentioned earlier. For composite materials, again, different results can be found dependent on the type of composite but usually as reinforcement increase, the peak height decreases and the peak width at half-height increases. In Fig 3 b) can be observed that as the reinforcement increases, narrower is the curve width. But in some cases, the curve is broaden by reinforcement content vii) activation energy – according to the references data obtained this parameter is dependent of the fiber length, reinforcement content and the type of fibers used (also hybridization). In general, the activation energy seems to increase as T_g does.

5. Conclusion

The absence of a significant variation in both glass transition temperature and activation energy values for composite materials does not allow the application of the fragility concept as proposed in literature based on WLF and VFT equations; there are an overestimation of the fragility index. In studying the normalized dynamic mechanical curves the behavior of the curves after the glass transition temperature, does not show any clear trend in comparing

different composite families. However, for qualitatively comparison dynamic fragility behavior can be applied but carefully.

Acknowledgement

The authors would like to thank CAPES, CNPQ for financial support.

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